"SYNTHESIS AND CHARACTERIZATION OF CALCIUM PHOSPHATE-ALUMINA COMPOSITES "

A THESIS SUBMITTED IN PARTIAL FULFILMENT AS A REQUIREMENT FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

By

ASHISH KUMAR PANDA
Roll No: 108CR037

DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA
2011-2012

"SYNTHESIS AND CHARACTERIZATION OF CALCIUM PHOSPHATE-ALUMINA COMPOSITES "

A THESIS SUBMITTED IN PARTIAL FULFILMENT AS A REQUIREMENT FOR THE DEGREE OF BACHELOR OF TECHNOLOGY

By

ASHISH KUMAR PANDA
Roll No: 108CR037
Under the Guidance of
Prof. SUDIP DASGUPTA

DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA
2011-2012

CERTIFICATE

This is to certify that the project entitled, ***"Synthesis and Characterization of Calcium Phosphate-Alumina Composites "*** submitted by **Ashish Kumar Panda (Roll No. 108CR037)** is an authentic work carried out by him under my supervision and guidance for the partial fulfilment of the requirements for the award of **Bachelor of Technology Degree** in **Ceramic Engineering** at **National Institute of Technology, Rourkela.**

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of any Degree or Diploma.

Prof. Sudip Dasgupta
Department of Ceramic Engineering
National Institute of Technology
Rourkela-769008

ACKNOWLEDGEMENT

I would like to express my heartfelt thanks and gratitude to Professor Sudip Dasgupta, Department of Ceramic Engineering, NIT Rourkela, my guide and my mentor, who was with me during every stage of the work and whose guidance and valuable suggestions has made this work possible.

Further, I would also like to thank all the faculty members and staff of Department of Ceramic Engineering, NIT Rourkela for their invaluable support and help during the entire project work.

I would further like to thank all the research scholars, for their round the clock help and support during the entire project work.

And finally, my hearty thanks to all my friends who have constantly helped me.

ASHISH KUMAR PANDA
(108CR037)

11TH MAY 2012

ABSTRACT

In the present study synthetic α-alumina and calcium phosphate based composites were processed and their mechanical properties were characterized. α-Alumina nano-powder was synthesized using reverse micelle method. Calcium phosphate nano-powders with different molar ratio starting from 1.8 to 1.1 was synthesized by precipitation method, using calcium nitrate ($Ca(NO_3)_2.4H_2O$) and ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) as precursor materials as source for calcium (Ca^{2+}) and phosphate ($(PO_4)^{3-}$) ions respectively. Then 5, 10, 20 weight % of Calcium phosphate powder was mixed with alumina, consolidated and sintered at 1400°C for 4 hours. The synthesized composites, in form of pellets were characterized for bulk density, apparent porosity, hardness and flexural strength and its grain size and morphology were studied from SEM micrographs of sintered pellets.

The synthesized composites were found to have a bulk density in the range 3.092 – 3.76 g/cc, apparent porosity in the range 11-20% and hardness in the range 193.3 - 335 HV.

CONTENTS

	Page No
Acknowledgement	***i***
Abstract	***ii***
CHAPTER 1: INTRODUCTION	**1**
CHAPTER 2: LITERATURE REVIEW	**4**
2.1 Scope of Ceramic Biomaterials	5
2.2 Bioceramics	6
2.3 Alumina as a Bioceramic material	8
2.4 Calcium Phosphate based Bioceramic material	8
2.5 Preparation of Calcium Phosphate	11
2.6 Preparation of α –Alumina	12
CHAPTER 3: EXPERIMENTAL PROCEDURE	**13**
3.1 Preparation of Calcium Phosphate Powder	14
3.2 Preparation of α - Alumina Powder	15
3.3 Preparation of Calcium phosphate –Alumina composites	16
3.4 Characterization	16
CHAPTER 4: RESULTS & DISCUSSIONS	**20**
4.1 X-Ray Diffraction pattern of Calcium Phosphate powder	21

4.2 Particle Size Analysis of Calcium Phosphate Powders 21

4.3 X-Ray Diffraction Pattern of Alumina Powder 25

4.4 Bulk Density of Sintered Composites 26

4.5 Apparent Porosity of Sintered Composites 29

4.6 Hardness of Sintered Composites 31

4.7 Bi-Axial Flexural Strength of Sintered Composites 33

4.8 SEM of Sintered Composites 37

CHAPTER 5: CONCLUSIONS & SCOPE FOR FUTURE WORK 38

REFERENCES 40

CHAPTER 1

INTRODUCTION

For the last 40 years, ceramics materials are increasingly being used for the repair and reconstruction of skeletal diseases and disorders. The term bioceramics are being used for those manmade materials which are being used as medical implant and exhibit specific positive response within the body aimed for the repair or augmentation of damaged tissue and/or skeletal parts. These bioceramic materials particularly calcium phosphate based materials are being preferred mainly as bone substitute or scaffolds due to its biocompatibility, better bone and tissue bonding ability, and its compositional similarity with the inorganic components of human bone. Many of these bioceramic materials also possess excellent chemical resistance, compressive strength and wear resistance. However, there are some bioceramic materials which are inert in their bioactive response. This implies that the "bioinert" biomaterials lacks strong bond at the interface between the implant and the host tissue and are bonded through a fibrous capsule of non-adhering tissue.

Calcium phosphate based ceramics has a wide range of composition where phases are either bio-active or bio-resorbable and hence finds wide range application in repairing masculoskeletal disorder as well as bone augmentation in defect or diseased side of human body. Calcium phosphate-based materials have attracted considerable interest in orthopaedic and dental applications because of their biocompatibility and tight bonding to bone, resulting in the growth of healthy tissue directly onto their surface. Among them, Apatite has been investigated as an alternative biomedical material. Apatite has also been considered as an attractive material for its similarity in structure and composition to bone. In vitro studies have shown that apatite is biocompatible, has a better stability and ensures the formation of a mechanically and functionally strong bone. However, the mechanical properties of apatite and all other calcium phosphates are generally inadequate for many load-carrying applications. These bioceramics have a low density, decreasing the mechanical properties of

the implant. Several combinations between calcium phosphate and other compounds have been proposed in order to improve the poor mechanical properties of calcium phosphate.

Alumina (α-Al_2O_3) was the first bioceramic widely used clinically. It is used in load-bearing hip prostheses and dental implants because of its combination of excellent corrosion resistance, good biocompatibility, high wear resistance and high strength. Alumina is reported to be bio-inert until its grain size is in nano scale.

The aim of this work was to elaborate a dense material having adequate mechanical properties to be used essentially as dental implants. Implants present the quality of auto-protection against caries proliferation.

This work focuses on preparing biphasic Calcium phosphate - α –Alumina composites, to investigate on the sintering behaviour and as a whole is to characterize the physical and mechanical properties of the nano composite.

CHAPTER 2

LITERATURE REVIEW

2.1 Scope of Ceramic Biomaterials:

Only a few of the materials known satisfy the requirements of implantation in the body. These biomaterials belong to all 5 major classes of materials: metals, ceramics, polymers, composites and natural materials. Wide diversity of these materials used in medicine is a result of materials research done in the last 50 years by controlling the composition, purity, physical properties of the materials and synthesizing new materials with new and special properties. These biomaterials are tailored according to the needs of medical devices such as woven polymer fibers in vascular grafts, bundles of cellulose acetate fibers in artificial kidney dialyzers, and titanium alloys in hip replacements **[1]**. The common property of all the biomaterials is biocompatibility or non-toxicity which is the definition of a material that is not recognized by the body as a potentially harmful foreign substance. Body can react instantly to a foreign material by the cells in body fluid and start an inflammation reaction followed by a wound healing process. Once an implant is placed in the body, an injury response is initiated by the tissue that results in inflammation as a reaction to local injury. Injury at the implant site leads to immediate development of the provisional matrix which consists of fibrin and inflammatory products released by the activated platelets, inflammatory cells and endothelial cells. Not all biocompatible materials are inert in the body but the highly bioactive ones incorporate to the actions of body like providing a host matrix for tissue growth or being slowly replaced by the growing tissue. Biocompatible materials are classified as bioinert, resorbable and bioactive according to tissue response. Bioinert materials induce formation of a fibrous tissue of variable thickness, interfacial bond forms on bioactive materials, and resorbable materials are replaced by the surrounding tissue **[1]**. Materials capable of evading attack by the body's immune system, and of stimulating tissue growth, are potentially far more effective and less costly. Mechanical similarity of the biomaterial to the host or replaced tissue is another important property. Especially in hard tissue replacements

the biomaterial is required to support or share a portion of the load. Compressive strength, fracture toughness and hardness of biomaterials are important in these cases.

2.2 Bioceramics:

Ceramics materials in form of oxides are the most commonly used and also found in great quantities in nature. The chemical synthesis, shaping and heat treatment processes of oxides are relatively simple compared to other materials. The properties common to all ceramics are chemical stability, low density, high hardness, low tensile strength and high compressive strength. Ceramics are ideal materials for mobile load bearing components in aggressive environments such as engine blocks, refractories and hard tissue replacements. Body is an active system regularly maintaining itself with its defense mechanism for optimum working conditions. A continuous process of building up and breaking down biostructures provides a demanding aggressive environment for body components. The actions of living cells as a part of the immune system are on the nanoscale and are basically chemical dissolution and adsorption processes. Following contact with body tissue, bare surface of a biomaterial is covered rapidly with proteins that are adsorbed from the surrounding body fluids. The chemistry of the underlying substrate, due to its effect on wettability and surface charge, controls the nature of the adherent protein layer. Macrophage fusion and platelet adhesion are strongly dependent on surface chemistry **[1]**. Although cells are able to adhere, spread and grow on bare biomaterial surfaces in vitro, proteins adsorbed from the adjacent tissue environment and adherent cells enhance cell attachment, migration and growth. Cell adhesion to biomaterials is mediated by cytoskeletal associated receptors in the cell membrane which interact with cell adhesion proteins that adsorb to the material surface from the surrounding plasma. The chemical nature of a biomaterial placed in the body as an implant therefore is

important in functioning of the body. Some ceramics that have been tested in vivo do not cause increased activity of immune system when dissolved in body fluid or in contact with tissues. Such ceramics, mainly oxides, are termed bioceramics. Bioceramics have the advantage of being compatible with the human body environment. Their biocompatibility is a direct result of their chemical compositions which contain ions commonly found in the physiological environment such as Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, and of other ions showing very limited toxicity to body tissues (such as Al^{3+} and Ti^{2+}). Due to their excellent tribological properties and with their improved fracture toughness and reliability, structural ceramics such as polycrystalline alumina and has been used as hard tissue replacement materials . One remarkable success of bioceramics as implant materials over the last two decades has been the emergence and clinical use of bioactive ceramics that elicit a specific biological response at the interface of the material resulting in the formation of a strong bond between the tissue and the material. These bioceramics include calcium phosphates with hydroxyapatite being the prominent family member, Bioglasss, A-W glass–ceramic, and other bioactive glasses and glass–ceramics. However, the brittle nature of ceramics such as alumina and the low strength of bioactive ceramics such as hydroxyapatite have limited their scope of clinical applications. Bioceramics are generally used to repair or replace skeletal hard tissues and their stable attachment to connective tissue varies significantly. Bioceramics can be classified into four groups based on their type of attachment to the surrounding tissues. Dense and nearly inert ceramics attach to the bone by morphological fixation, or growth of bone into surface irregularities. Porous and inert ceramics are attached to the bone by ongrowth of the tissue or biological fixation. Dense and surface reactive ceramics attach directly by chemical bonding to the bone or bioactive fixation. Resorbable ceramics attach to the bone by any of the above mechanisms and are slowly replaced by bone. Examples to each of these types of

bioceramics are Al_2O_3, HA coated porous implants, hydroxyapatite, and tricalcium phosphate respectively.

2.3 Alumina as a Bioceramic material:

Biocompatible ceramics with mechanical properties comparable to metals are preferred in parts of the body that have high wear risk. An inert ceramic, alumina is used in load bearing hip prosthesis and dental implants in dense and pure state because of its excellent corrosion resistance, high strength and high wear resistance **[9]**. Alumina's long term use in orthopedic surgery has been motivated by its excellent biocompatibility and very thin capsule formation which permits cementless fixation of prostheses as well as its very low coefficients of friction and wear. As a mechanically strong ceramic, alumina is also used as a reinforcing material in biocomposites. Clinical applications of alumina include knee prostheses, bone and dental screws, alveolar ridge and maxillofacial reconstruction, acicular bone substitutes, corneal replacements and segmental bone replacements.

2.4 Calcium Phosphate based Bioceramic material:

The main crystalline component of the mineral phase of bone is calcium deficient carbonate-hydroxyapatite. Similarity of synthetic hydroxyapatite to bone mineral makes it the most clinically used biomaterial. Hydroxyapatite has a hexagonal symmetry and unit cell lattice parameters a = 0.95 nm and c = 0.68 nm. Taking into account the lattice parameters and its symmetry, its unit cell is considered to be arranged along the c-axis. This would justify a preferred orientation that gives rise to an oriented growth along the c-axis and a needle-like morphology **[2]**. Hydroxyapatite belongs to calcium phosphate class that is characteristically

resorbable in body. Tetracalcium Phosphate ($Ca_4P_2O_9$), Amorphous calcium Phosphate, Tricalcium Phosphate ($Ca_3(PO_4)_2$), and Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) are members of calcium phosphates in order of decreasing solubility in body fluids. Unlike the other calcium phosphates, hydroxyapatite does not break down under physiological conditions. In fact, it is thermodynamically stable at physiological pH and actively takes part in bone bonding, forming strong chemical bonds with surrounding bone. For bone mimetic implants synthetic hydroxyapatite is produced by various methods. Hydroxyapatite is a thermally unstable compound, decomposing at temperatures from about 800-1200°C depending on its stoichiometry. The stoichiometry of hydroxyapatite is highly significant if thermal processing of the material is required **[2]**. Calcium phosphate phases of alpha and beta-tricalcium phosphate, tetracalcium phosphate occur with slight imbalances in the stoichiometric ratio of calcium and phosphorus in HA from the molar ratio of 1.67. It is also important to know the close relation between the stoichiometry, acidity and solubility. Thus, it is known that the lower the Ca/P ratio and the larger the acidity of the environment, the higher will be the solubility of the HA. For Ca:P < 1, both acidity and solubility are extremely high, and both parameters decrease substantially for Ca/P ratios close to 1.67, which is the value of stoichiometric hydroxyapatite **[3]**. The prevention of the formation of calcium phosphate phases with relatively higher solubility is significant when stability of hydroxyapatite is an important issue in the application. It is possible to sinter phase pure hydroxyapatite using stoichiometric composition at temperatures up to 1300°C. Hydroxyapatite lacks the mechanical strength required for long term use in biomedical implants **[10]**. In practice hydroxyapatite is either used as a bioactive coating on implants or reinforced by metal or ceramic phases. Several techniques have been utilized for the preparation of hydroxyapatite **[2,3,5]**. Materials with various morphology, stoichiometry, and level of crystallinity have been obtained depending on the technique. The synthetic routes employed can be divided into

solid-state reactions and wet methods, which include precipitation, hydrothermal and hydrolysis of other calcium phosphates. Modifications of these "classical" methods (precipitation, hydrolysis or precipitation in the presence of urea) or alternative techniques have been employed to prepare hydroxyapatite with morphology, stoichiometry, ion substitution or degree of crystallinity as required for a specific application. A stoichiometric and well crystallized product with low sinterability is obtained with wet methods but relatively high temperatures and long heat treatment times are required in synthesis **[4]**. Nanometer sized crystals can be obtained at temperatures lower than 100°C with precipitation techniques in the shape of needles, rods or equiaxed particles. Their crystallinity and stochiometry is close to well crystallized stoichiometric HA under precise control of preparation conditions. A common method of precipitation synthesis of HA is by using calcium nitrate and ammonium phosphate in the presence of ammonium hydroxide. Hydrothermal techniques give hydroxyapatite powders with a high degree of crystallinity and better stoichiometry having a wide distribution of crystal sizes. Applications of hydroxyapatite include surface coating of orthopedic and dental metal implants where HA both promote osteointegration process and reduce metal ion release by acting as a physical barrier; bioceramic preparation for replacements of bone fragments, repair of periodontal bony defects; and use as drug carrier for controlled drug release with promising potential to heal bone fractions and suppress inflammation process. Hydroxyapatite has been used clinically in different applications **[2-3]**. It has been utilized as a dense, sintered ceramic for middle ear implants, alveolar ridge reconstruction and augmentation, in porous form as granules for filling body defects in dental and orthopaedic surgery and as a coating on metal implants.

2.5 Preparation of Calcium Phosphate (Apatite):

- **Precipitation Method**

  The precursors used are calcium nitrate tetrahydrate as the source of calcium and ammonium dihydrogen orthophosphate as the source of phosphate. Ammonia solution is used as precipitant and it is added to maintain a pH of 10. It has been reported that the hydroxyapatite prepared through this technique shows excellent mechanical properties.

  $Ca(NO_3)_2.4H_2O + NH_4H_2PO_4 + NH_4OH \longrightarrow Ca_{10}(PO_4)_6(OH)_2$

- **Hydrothermal method**

  Calcium carbonate is used as the source for calcium and Ammonium dihydrogen orthophosphate is used as the source for phosphate.

  $CaCO_3 + NH_4H_2PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + H_2O + CO_2$

- **Solid State Synthesis**

  The precursors used in the preparation of hydroxyapatite are calcium hydroxide as the source of calcium and phosphoric acid as the source of phosphate **[5]**.

  $Ca(OH)_2 + H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2$

2.6 Preparation of α –Alumina:

Nano sized alumina powders are prepared by Reverse Micelle process **[6]**.

By stepwise hydrolysis, using aqueous ammonia as the precipitant, hydroxide precursor is obtained from nitrate solutions dispersed in nano sized aqueous domains of micro emulsion consisting of Cyclohexane as the oil phase, Triton-X as the non-ionic surfactant and aqueous solution containing Aluminium nitrate as the water phase. Butanol is taken as the co-surfactant.

$$Al(NO_3)_3.9H_2O + NH_4OH \longrightarrow Al(OH)_3 + NH_4NO_3$$

Now the precipitate is washed properly and then calcined at 1200°C to obtain α-alumina nano powder.

CHAPTER 3

EXPERIMENTAL

PROCEDURE

3.1 *Preparation of Calcium Phosphate Powder:*

Calcium phosphate required in the study was prepared by **precipitation method**. Six different batches of calcium phosphate with varying Ca/P molar ratio (1.8, 1.67, 1.5, 1.33, 1.21 and 1.1) were synthesized. Calcium nitrate ($Ca(NO_3)_2.4H_2O$) and ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) were taken as precursor materials as source for calcium (Ca^{2+}) and phosphate ($(PO_4)^{3-}$) ions respectively. Ammonia solution was taken as the precipitant.

Molar weight of $Ca(NO_3)_2.4H_2O$ = 236g

Molar weight of $NH_4H_2PO_4$ = 115g

For synthesis of each batch, the required weight ratios of the precursor materials are taken.

Ca/P Molar Ratio	Weight ratio of ($Ca(NO_3)_2.4H_2O$/ $NH_4H_2PO_4$) taken for synthesis
1.8	12.744 : 3.45
1.67	11.823 : 3.45
1.5	10.62 : 3.45
1.33	9.416 : 3.45
1.2	8.496 : 3.45
1.1	7.788 : 3.45

Table 3.1: Amount of precursors taken for synthesis of calcium phosphate nano powder with different Ca/P molar ratio

The amount of precursor materials taken are mixed properly and a solution is made. The PH of the solution is maintained at 10 by adding ammonia solution. The solution is stirred for 5-6 hours and after that it is allowed to precipitate. Then the precipitate is washed thoroughly by distilled water by centrifugal process in the Centrifuge apparatus.

Centrifuge cycle : 8000 rpm for 5 minutes

Each sample is washed properly for 3 times. Then finally each sample is dried in Vacuum drier at 80°C for 24 hours.

3.2 *Preparation of α - Alumina Powder:*

Nano sized alumina powders were synthesized via **Reverse Micelle process**.

200g of Aluminium nitrate ($Al(NO_3)_3.9H_2O$) was taken in 400ml water. 2000ml Cyclohexane was added to the aluminium nitrate solution and properly stirred. Now surfactant, Triton-X was added drop wise with continued stirring until a translucent or milky solution is formed. Then equal amount of co-surfactant, Butanol was added. Now the pH of the solution is maintained at 10 by adding precipitant, ammonia solution. The solution is properly stirred and allowed to precipitate. The precipitate was washed with Propan-2-ol and filtered with Whatman-40 filter paper.

$$Al(NO_3)_3.9H_2O + NH_4OH \longrightarrow Al(OH)_3 + NH_4NO_3$$

Now the filtrate is dried in Vacuum oven at 80°C and the dried powder is calcined at 1200°C to form alumina powder (Al_2O_3).

3.3 Preparation of Calcium phosphate –Alumina composites:

5, 10, 20 weight % of Calcium phosphate powder (6 batches) was mixed with Alumina powder separately to form composites with different composition. Each batch of composite was added with 3% PVA binder and pressed to form 0.5g of pellets in a 12mm cylindrical die. The green pellets are pressed at 4 Tonn pressure and given a dwell time of 90 seconds.

Now the green pellets were sintered at 1400°C with a soaking time of 4 hours.

The firing cycle was composed of 500°C with soaking time 2 hours, for binder burn out and 1400°C with 4 hours of soaking time, for sintering.

3.4 Characterization:

3.4.1 X-Ray Diffraction (XRD):

The XRD of calcium phosphate and alumina powder synthesized were done using Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu Kα radiation ($\lambda = 1.5406$ A°) at 40 kV and 30mA having a scan range(°2 θ) of 10-60° for calcium phosphate powder and 10-80° for alumina powder, at a scan speed of 0.04 (°2 θ/sec).

3.4.2 Particle Size Distribution Analysis:

Very little amount of calcium phosphate powder from each batch was taken and six different solutions were made. The solution were then set for ultrasonication using an unltrasonic vibratometer. Ultrasonication was done for 10 minutes until all the agglomerates were broken down. Now the particle size distributions of the calcium phosphate present in those solutions were done by using Malvern Particle Size Analyser.

3.4.3 Bulk Density (BD) and Apparent Porosity (AP):

The sintered pellets of the composite were immersed in water which was boiled for 3 hours until no vapours are seen coming out of the pellets. Now the dry, soaked and suspended weight of the pellets is calculated.

Bulk Density is calculated by the formula:

$$\text{Bulk Density} = \frac{Dry\ Weight}{Soaked\ Weight - Suspended\ Weight}\ x\ Density\ of\ the\ liquid$$

Apparent Porosity is calculated by the formula:

$$\text{Apparent Porosity} = \frac{Soaked\ Weight - Dry\ Weight}{Soaked\ Weight - Suspended\ Weight}\ x\ 100\%$$

3.4.4 Vickers Hardness (HV):

The sintered pellets of the composites were polished properly with Emery paper. Now the hardness of the pellets was measured by Vickers Hardness Tester.

Here an indent was given on the pellet and the lens of the instrument was focussed on the diameter of the indent.

Vickers hardness is given by the formula:

$HV = 1.854 * F/d^2$

where F is the indent given, measured in (KgF) and d is mean diameter of the indent measured in (mm)

3.4.5 Bi-axial Flexural Strength:

The diameter and thickness of the pellets were measured. Now the Bi-axial flexural strength of the pellets were measured by UTM machine. Here the pellets are kept on their width and a constant extension per time was fed in the instrument. The instrument measures the maximum load at fracture.

Flexural strength is given by formula:

$$\text{Flexural Strength} = \frac{2F}{\pi dt}$$

where F is the maximum load at fracture, d is diameter of the pellet and t is the thickness of the pellet

Sample no.	Composition
1	5% CaP (1.8) 95%Al_2O_3
2	5% CaP (1.67) 95%Al_2O_3
3	5% CaP (1.5) 95%Al_2O_3
4	5% CaP (1.33) 95%Al_2O_3
5	5% CaP (1.2) 95%Al_2O_3
6	5% CaP (1.1) 95%Al_2O_3
1’	10% CaP (1.8) 90%Al_2O_3
2’	10% CaP (1.67) 90%Al_2O_3
3’	10% CaP (1.5) 90%Al_2O_3
4’	10% CaP (1.33) 90%Al_2O_3
5’	10% CaP (1.2) 90%Al_2O_3
6’	10% CaP (1.1) 90%Al_2O_3
1’’	20% CaP (1.8) 80%Al_2O_3
2’’	20% CaP (1.67) 80%Al_2O_3
3’’	20% CaP (1.5) 80%Al_2O_3
4’’	20% CaP (1.33) 80%Al_2O_3
5’’	20% CaP (1.2) 80%Al_2O_3
6’’	20% CaP (1.1) 80%Al_2O_3

Table 3.2: Different composition of alumina-calcium phosphate composite

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 X-Ray Diffraction pattern of Calcium Phosphate Powders:

The X-Ray Diffraction pattern of the six batches of synthesized calcium phosphate nano powders is shown in the figure 4.1.

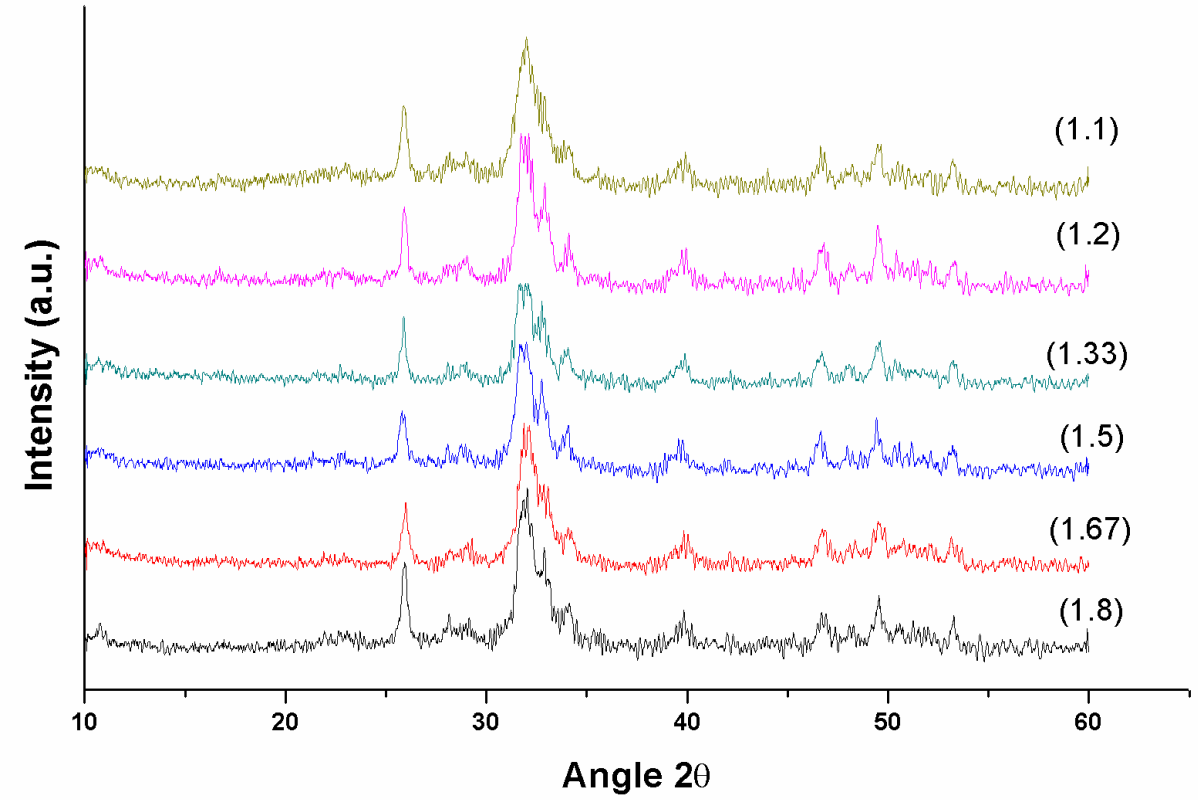

Fig 4.1: X-Ray Diffraction pattern for six batches of calcium phosphate

The X-Ray Diffraction pattern of the six different batches of calcium phosphate synthesized using precipitation method, with varying Ca/P molar ratio, shows the presence of hydroxy apatite phase.

4.2 Particle Size Analysis of Calcium Phosphate Powders:

The particle size distribution of the six batches of calcium phosphate is given below in figures 4.2a to 4.2f.

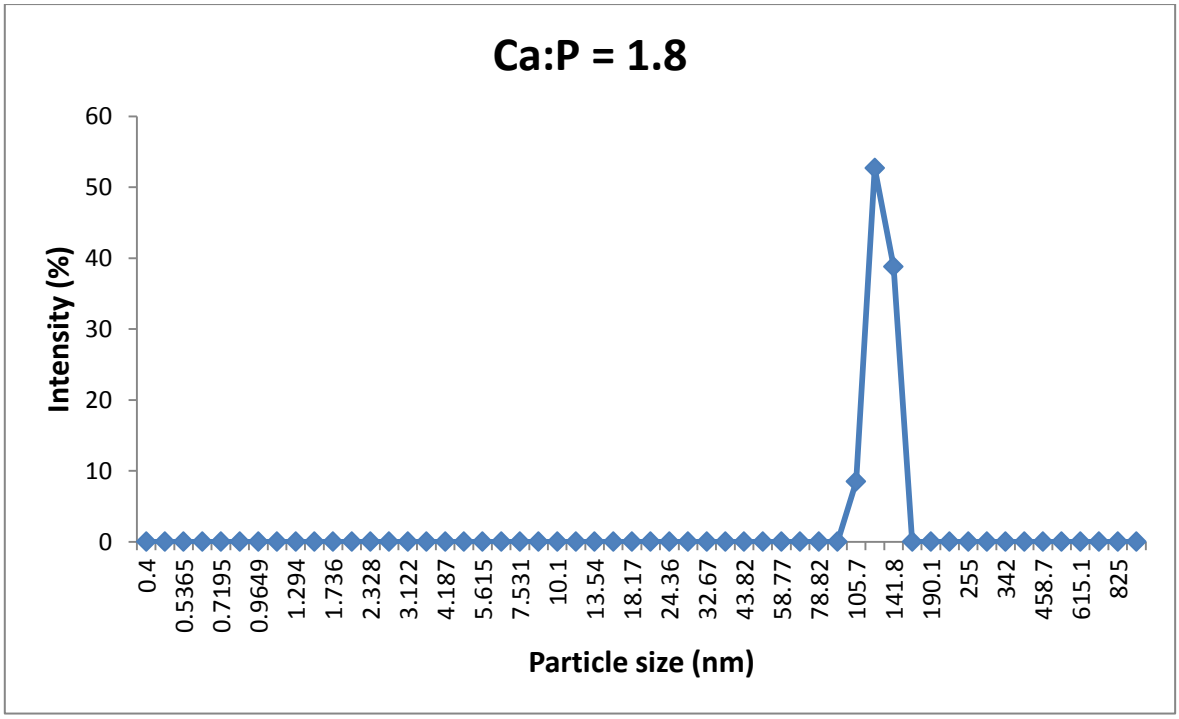

Fig 4.2a: Particle size distribution of Ca/P ratio = 1.8

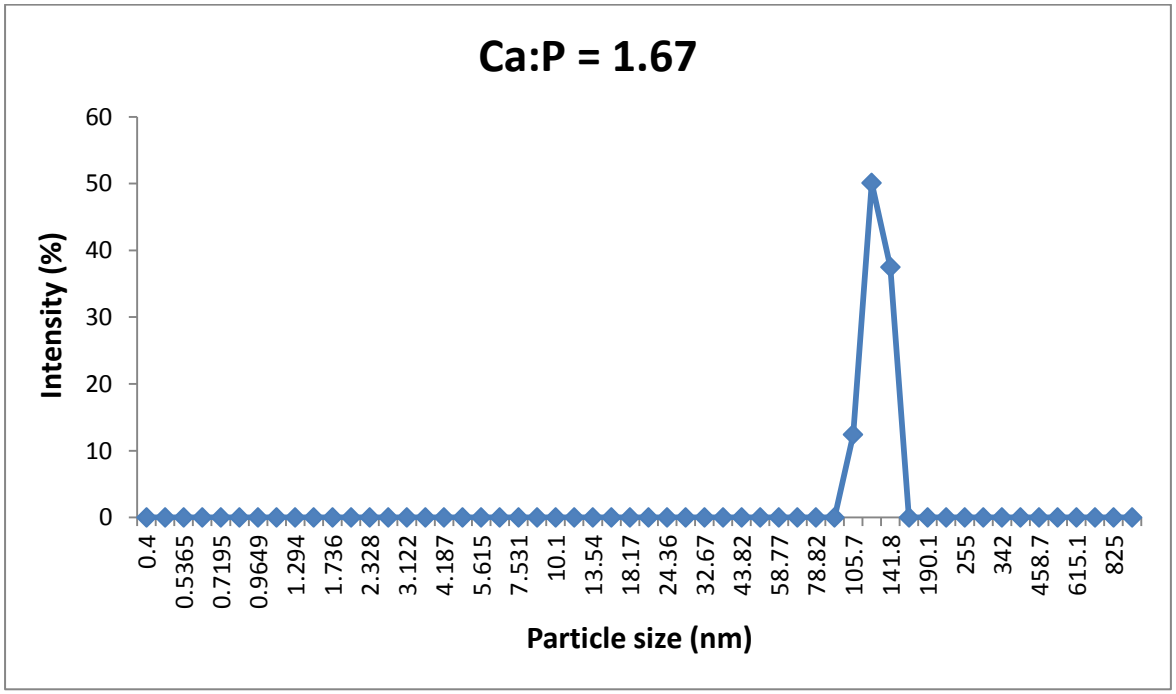

Fig 4.2b: Particle size distribution of Ca/P ratio = 1.67

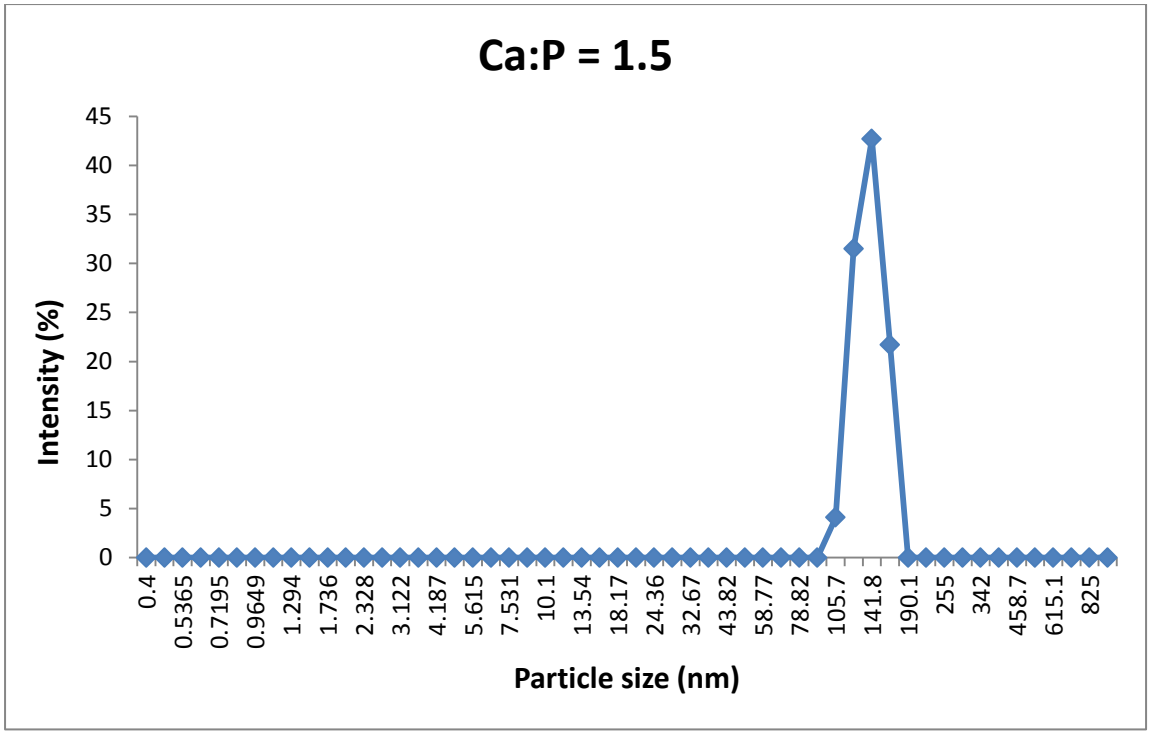

Fig 4.2c: Particle size distribution of Ca/P ratio = 1.5

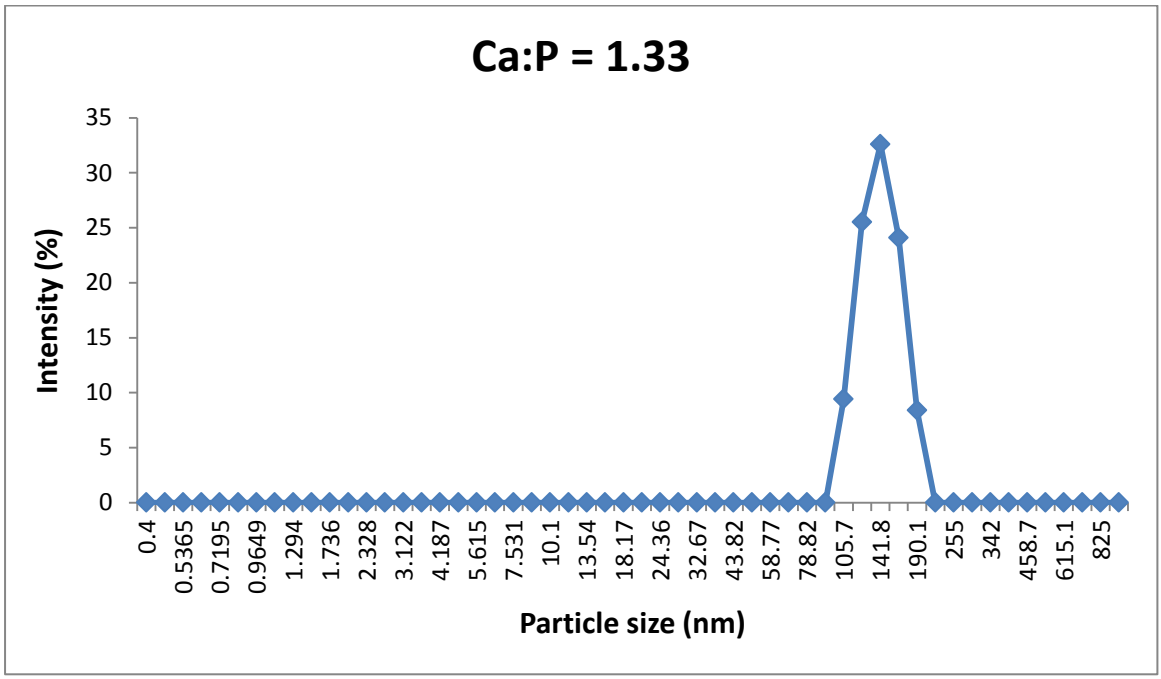

Fig 4.2d: Particle size distribution of Ca/P ratio = 1.33

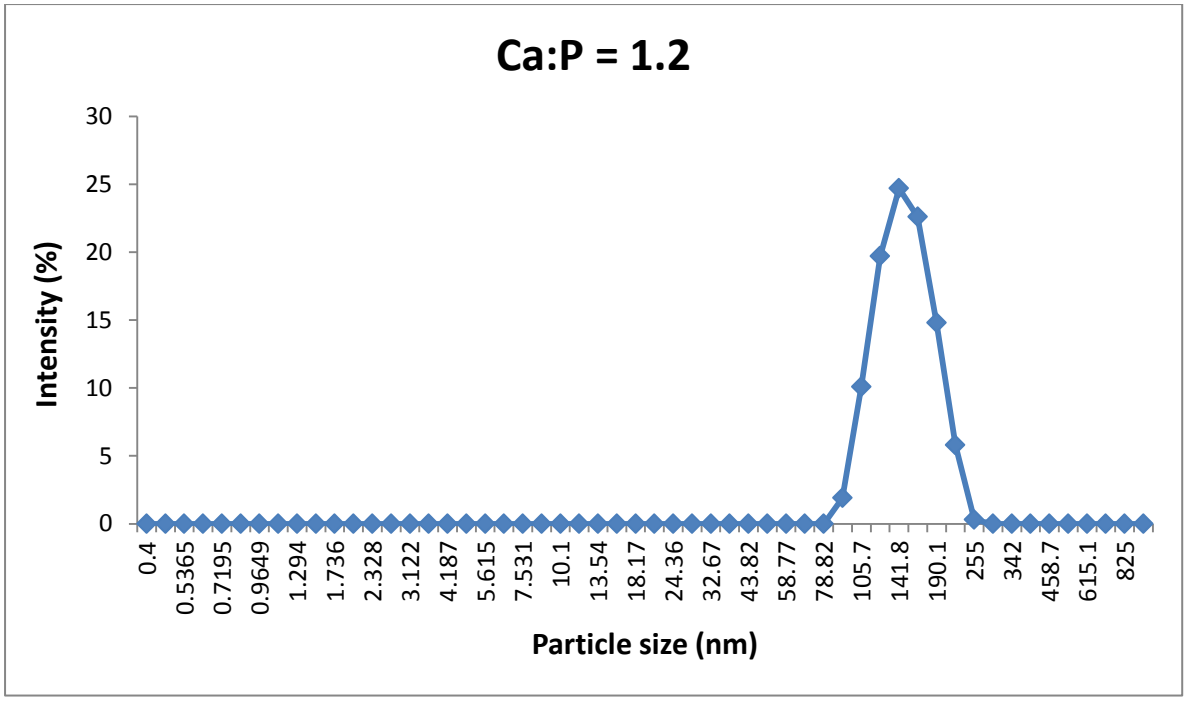

Fig 4.2e: Particle size distribution of Ca/P ratio = 1.2

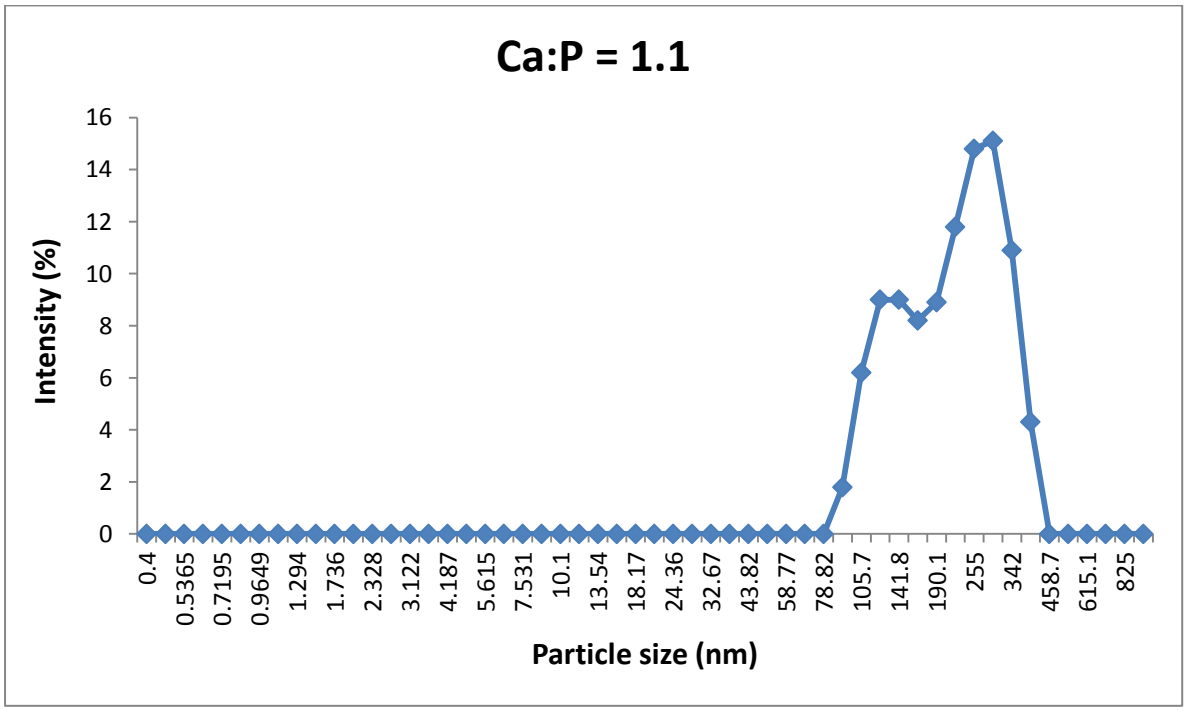

Fig 4.2f: Particle size distribution of Ca/P ratio = 1.1

The average particle size of the calcium phosphate nanopowders with Ca/P molar ratios 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 were found to be 128.51nm, 127.60nm, 139.07nm, 142.92nm, 150.33nm and 224.98nm respectively. The calcium phosphate nano powders with Ca/P molar ratio of 1.67 showed the lowest average particle size of 127.6 nm as shown in figure 4.2b and table 4.1.

Ca/P Ratio	Average Particle Size (nm)
1.8	128.51
1.67	127.60
1.5	139.07
1.33	142.92
1.2	150.33
1.1	224.98

Table 4.1: Average particle size of different calcium phosphate powders

4.3 X-Ray Diffraction Pattern of Alumina Powder:

The X-Ray diffraction pattern of alumina powder calcined at 1200°C for 4hrs is shown in figure 4.3.

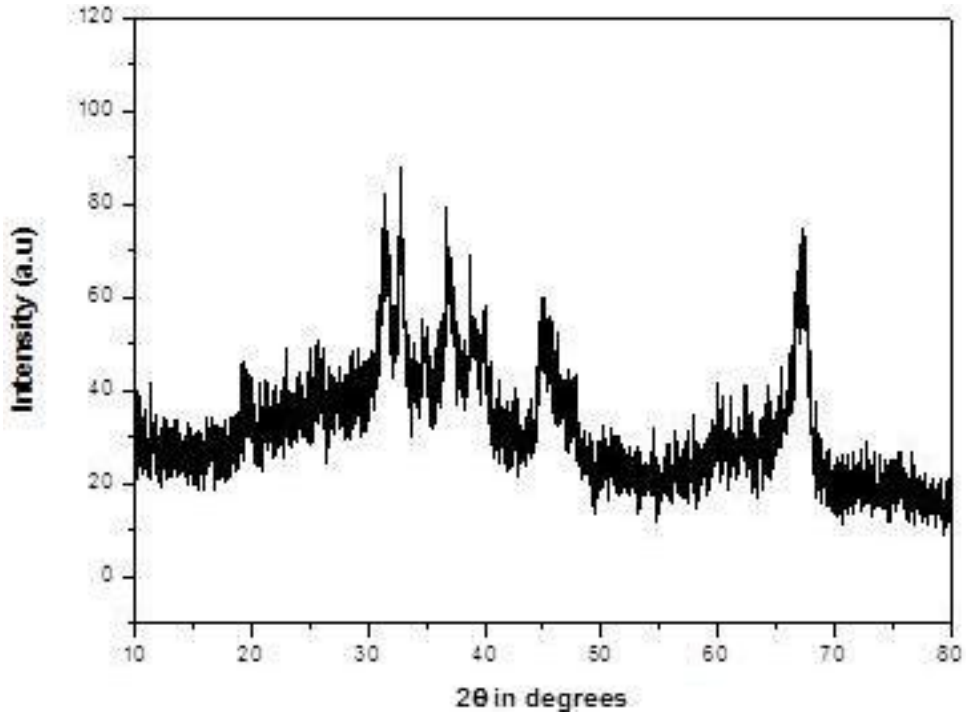

Fig 4.3: X-ray diffraction pattern of alumina powder calcined at 1200°C for 4hrs

The x-ray diffraction pattern of alumina powder synthesized using reverse micelle method and then calcined at 1200°C for 4hrs shows the presence of α-alumina.

4.4 Bulk density of sintered composite:

The bulk density distribution of the sintered calcium phosphate –alumina composite has been shown in figure 4.4a to 4.4c. The sample nos. 1, 2, 3, 4, 5 and 6 determines 5 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 95 weight % alumina powder as shown in figure 4.4a. Composition with Ca:P molar ratio of 1.67 showed the highest bulk density of 3.76 g/cc as shown in figure 4.4a.

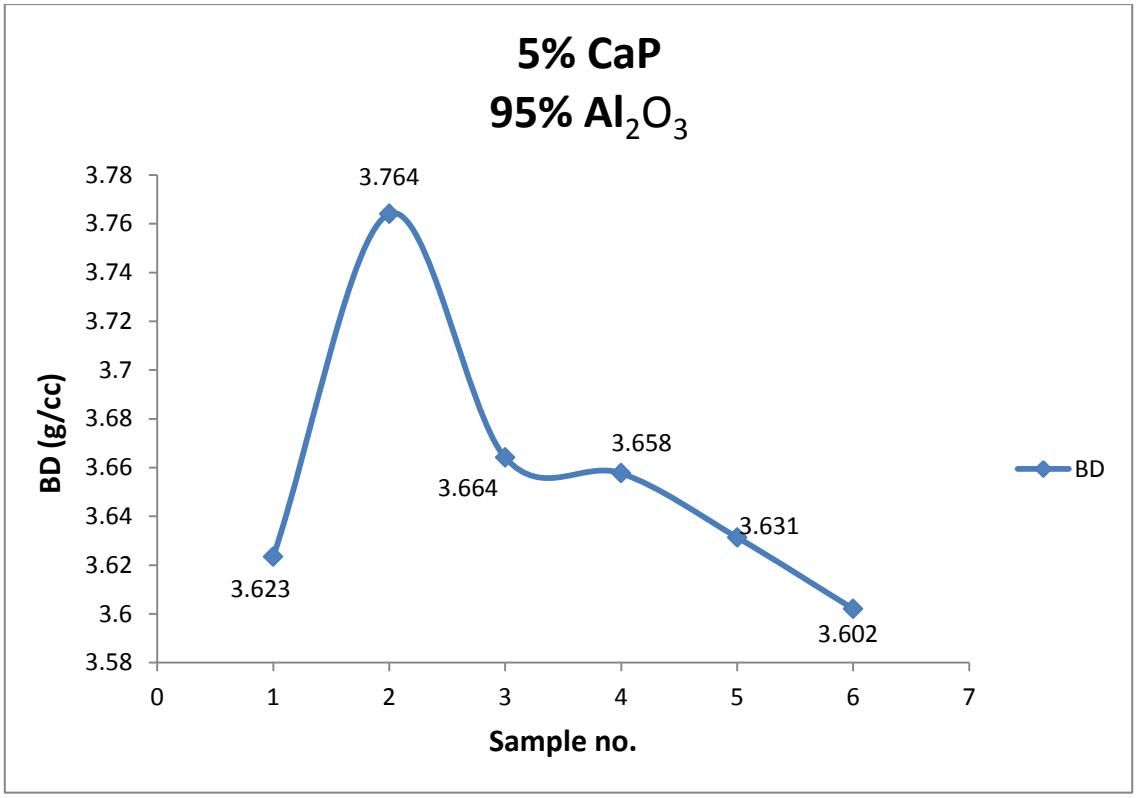

Fig 4.4a: Bulk density distribution for (5% CaP- 95% Al_2O_3) sintered composite

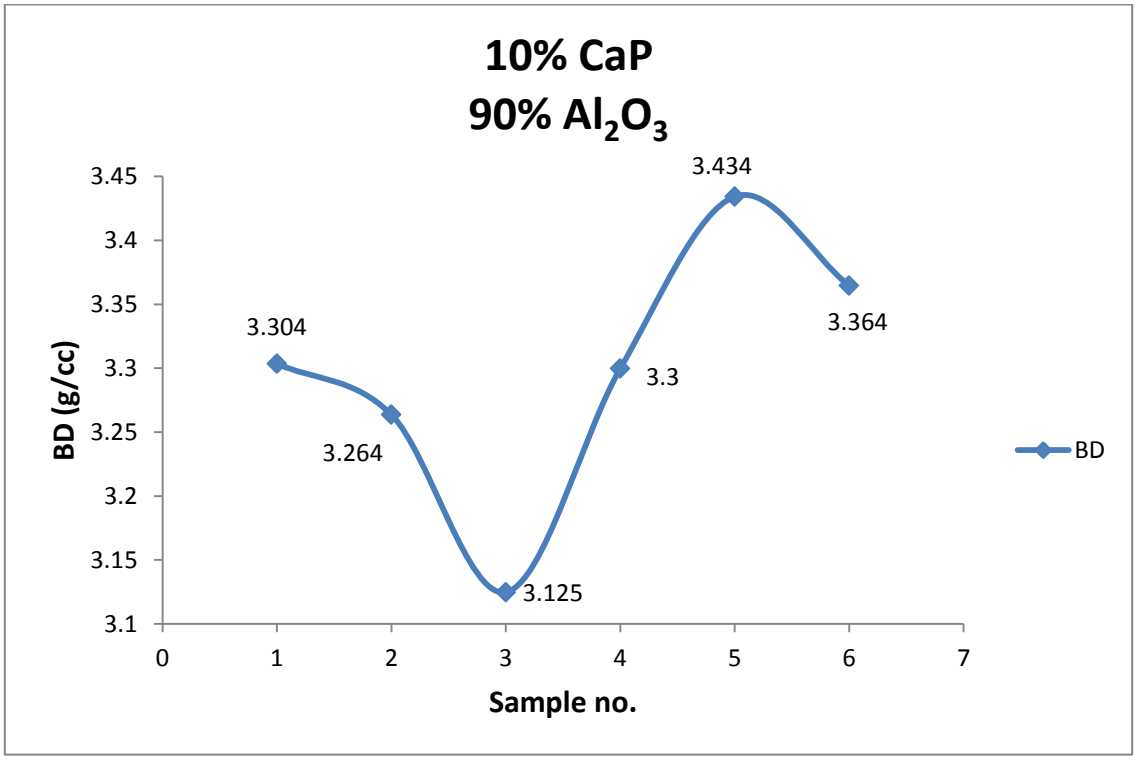

Fig 4.4b: Bulk density distribution for (10% CaP- 90% Al_2O_3) sintered composite

The sample nos. 1, 2, 3, 4, 5 and 6 in figure 4.4b determines 10 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 90 weight % alumina powder as shown in figure 4.4b. Composition with Ca:P molar ratio of 1.2 showed the highest bulk density of 3.43 g/cc as shown in figure 4.4b.

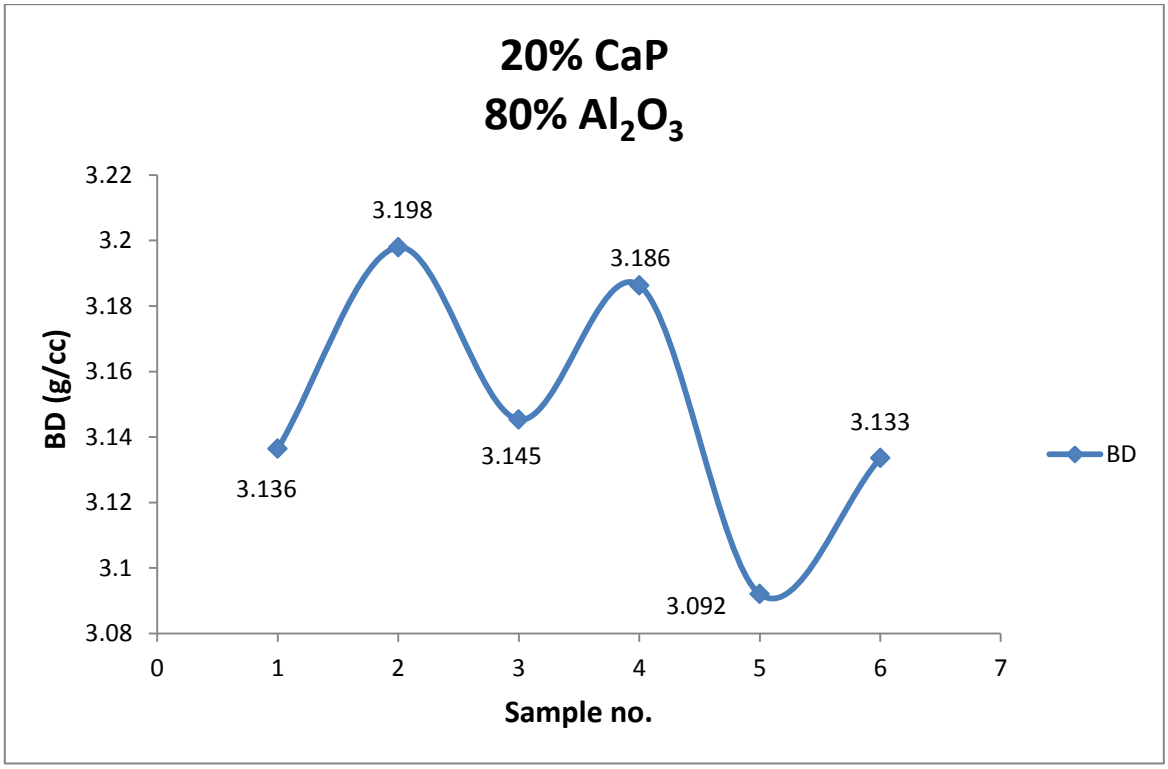

Fig 4.4c: Bulk density distribution for (20% CaP -80% Al_2O_3) sintered composite

The sample nos. 1, 2, 3, 4, 5 and 6 in figure 4.4c determines 20 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 80 weight % alumina powder as shown in figure 4.4c. Composition with Ca:P molar ratio of 1.67 showed the highest bulk density of 3.198 g/cc as shown in figure 4.4c.

4.5 Apparent Porosity of Sintered Composite:

The apparent porosity distribution of the sintered calcium phosphate –alumina composite has been shown in figure 4.5a to 4.5c. The sample nos. 1, 2, 3, 4, 5 and 6 determines 5 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 95 weight % alumina. Composition with Ca:P molar ratio of 1.67 showed the lowest apparent porosity of 11% as shown in figure 4.5a.

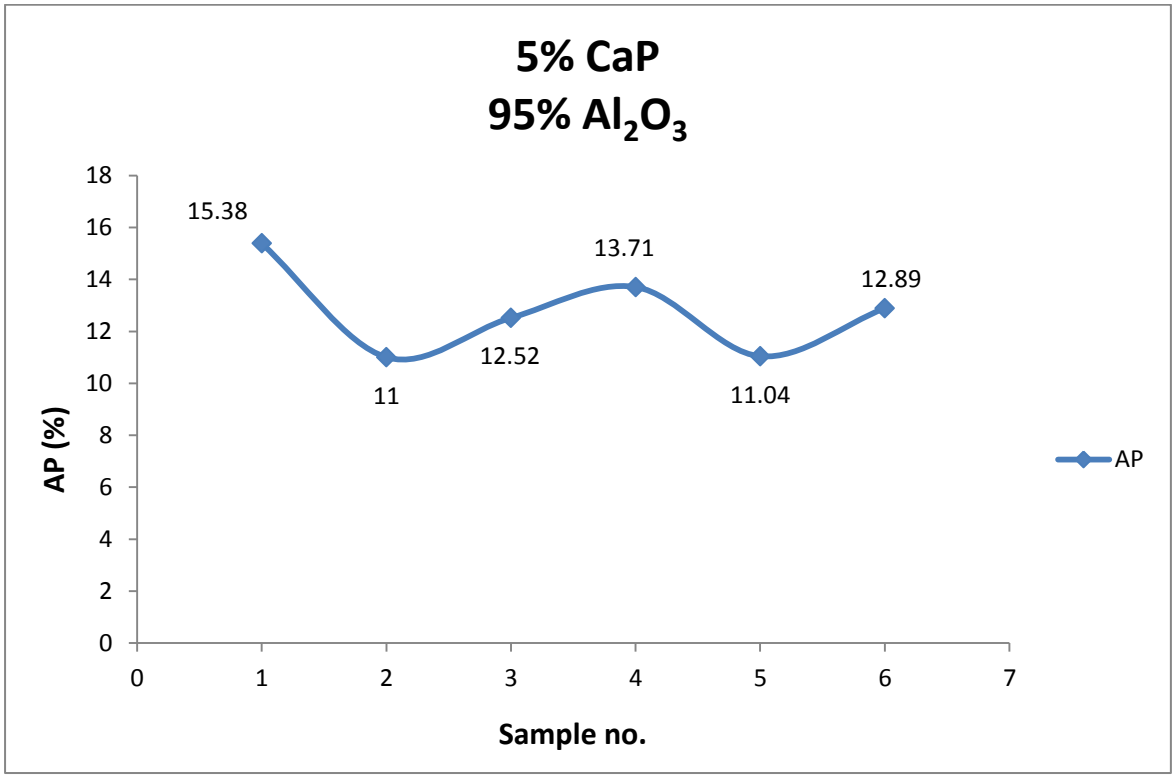

Fig 4.5a: Apparent porosity distribution for (5% CaP -95% Al_2O_3) sintered composite

. The sample nos. 1, 2, 3, 4, 5 and 6 determines 10 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 90 weight % alumina. Composition with Ca:P molar ratio of 1.2 showed the lowest apparent porosity of 13.75% as shown in figure 4.5b.

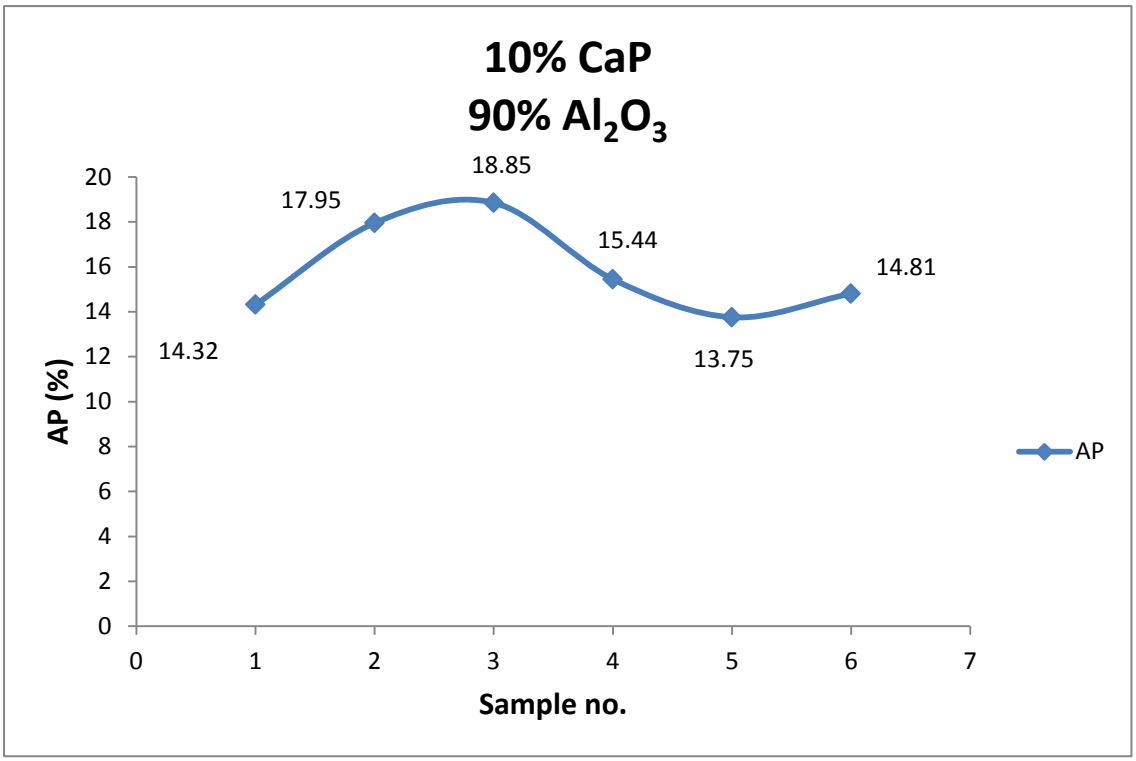

Fig 4.5b: Apparent porosity distribution for (10% CaP- 90% Al_2O_3) sintered composite

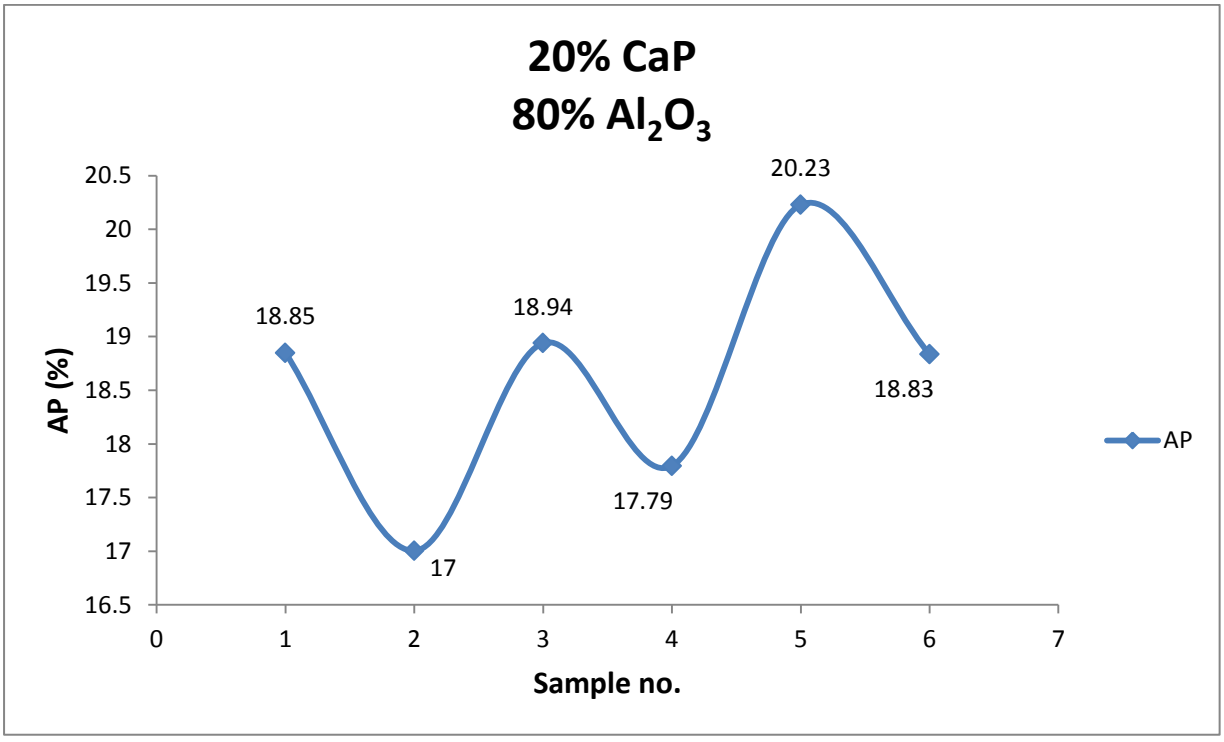

Fig 4.5c: Apparent porosity distribution for (20% CaP- 80% Al_2O_3) sintered composite

. The sample nos. 1, 2, 3, 4, 5 and 6 determines 20 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 80 weight % alumina. Composition with Ca:P molar ratio of 1.67 showed the lowest apparent porosity of 17% as shown in figure 4.5c.

4.6 Hardness of Sintered Composites:

The Vickers hardness distribution of the sintered calcium phosphate –alumina composite has been shown in figure 4.6a to 4.6c. The sample nos. 1, 2, 3, 4, 5 and 6 determines 5 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 95 weight % alumina. Composition with Ca:P molar ratio of 1.67 showed the highest hardness of 335 HV as shown in figure 4.6a.

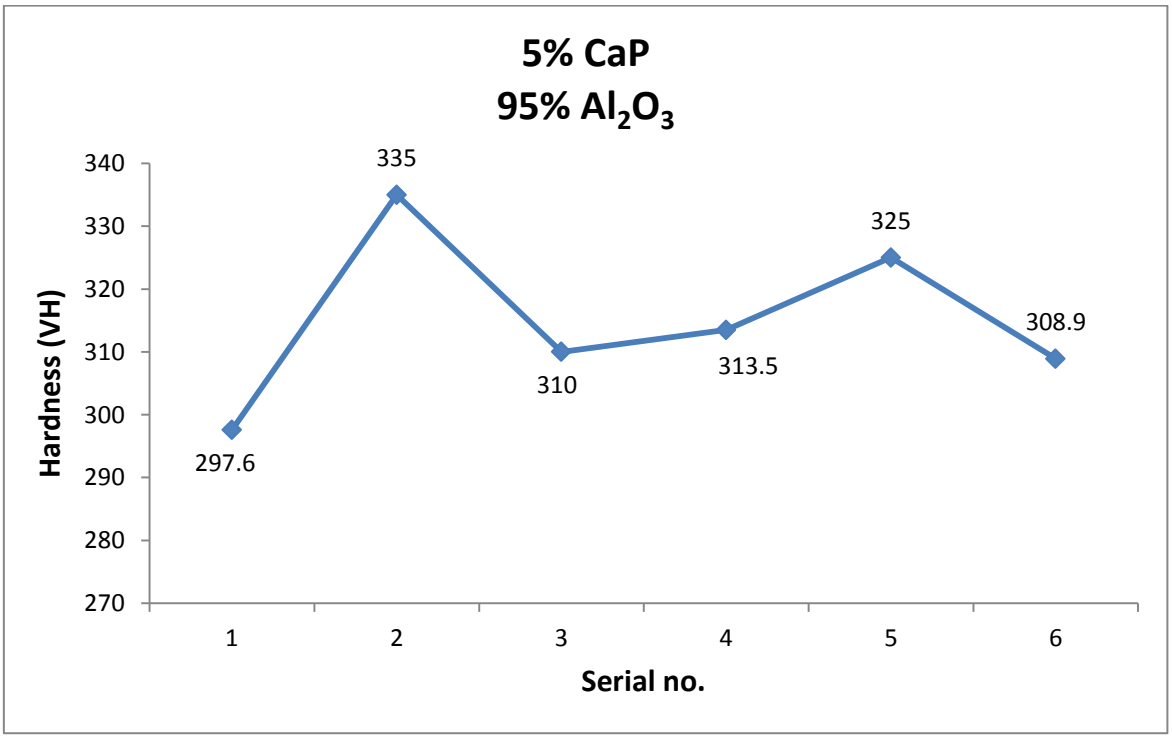

Fig 4.6a: Hardness distribution for (5% CaP- 95% Al_2O_3) sintered composite

The sample nos. 1, 2, 3, 4, 5 and 6 determines 10 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 90

weight % alumina. Composition with Ca:P molar ratio of 1.2 showed the highest hardness of 287.8 HV as shown in figure 4.6b.

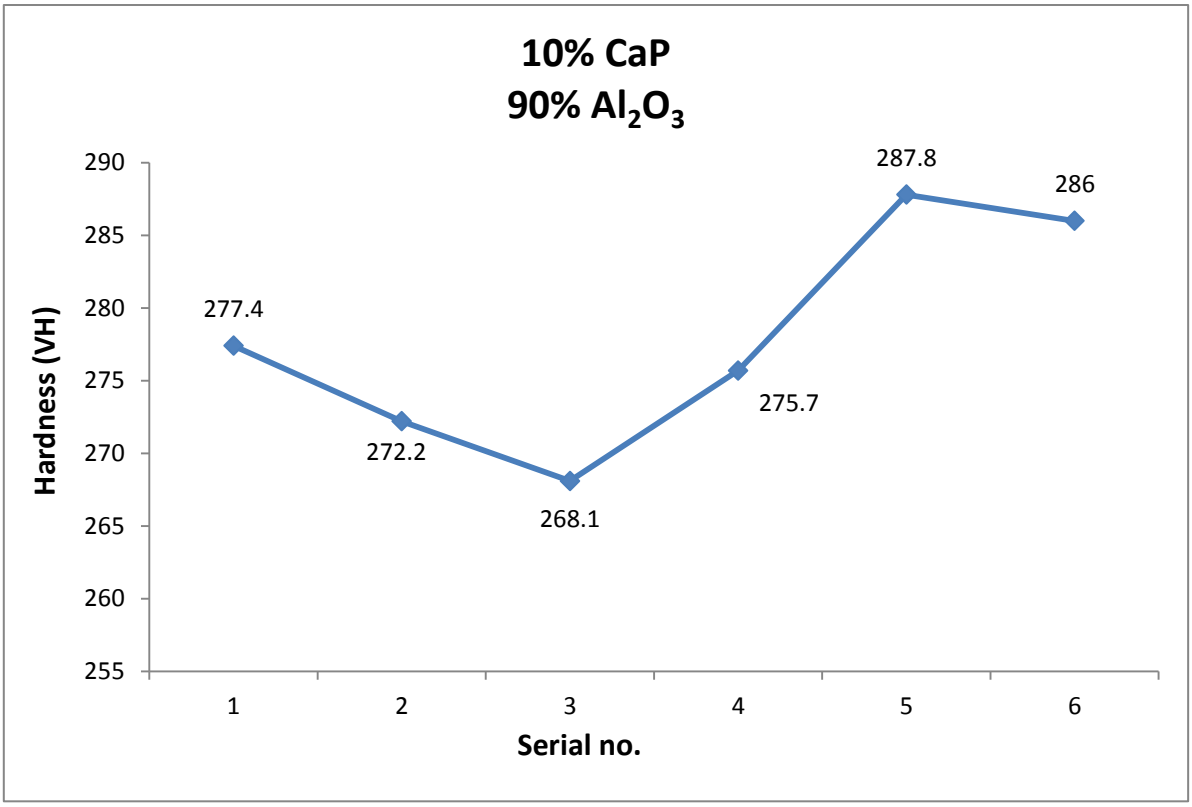

Fig 4.6b: Hardness distribution for (10% CaP- 90% Al_2O_3) sintered composite

The sample nos. 1, 2, 3, 4, 5 and 6 determines 20 weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 80 weight % alumina. Composition with Ca:P molar ratio of 1.67 showed the highest hardness of 222.4 HV as shown in figure 4.6c.

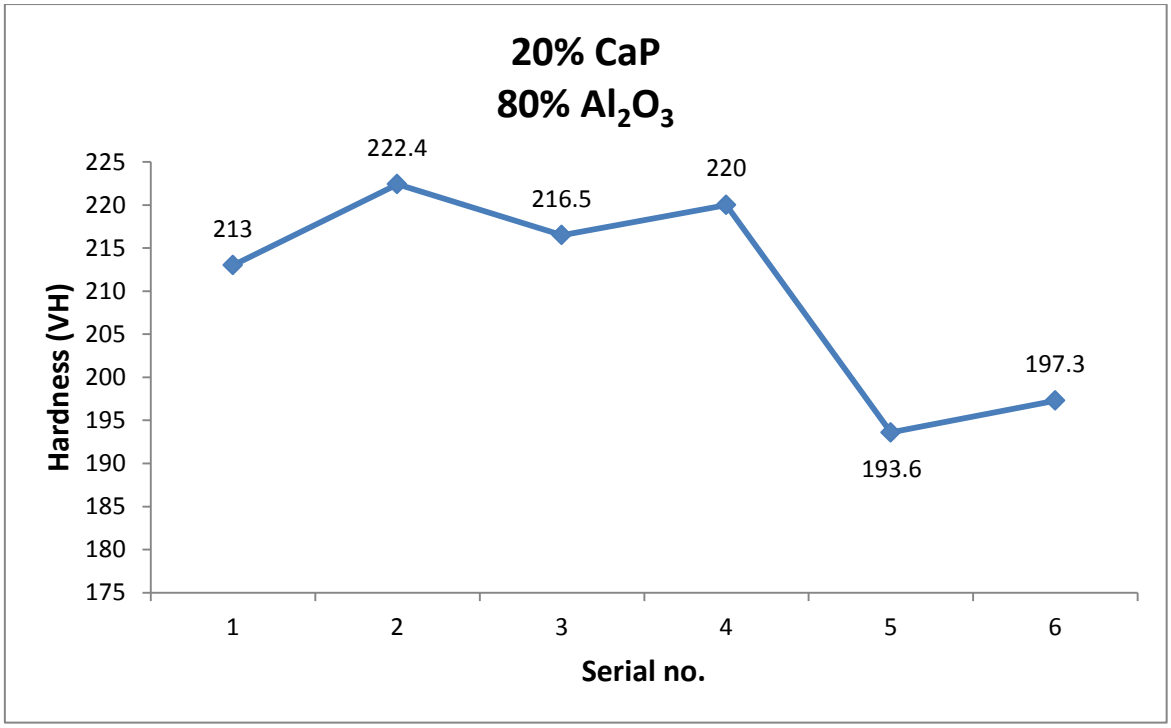

Fig 4.6c: Hardness distribution for (20% CaP -80% Al_2O_3) sintered composite

4.7 Bi-Axial Flexural Strength of Sintered Composites:

The load vs extension curve for 5% CaP(1.67)- 95% Al_2O_3 compact is shown in figure 4.7a.

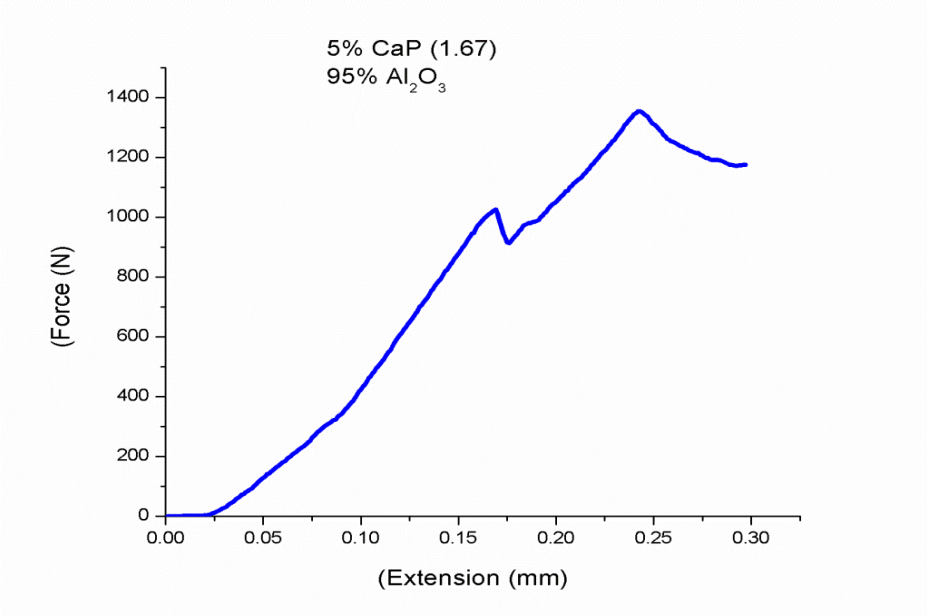

Fig 4.7a: Bi-Axial Flexural strength for (5% CaP(1.67)- 95% Al_2O_3) sintered composite

The load vs extension curve for 10% CaP(1.67)- 90% Al_2O_3 compact is shown in figure 4.7b.

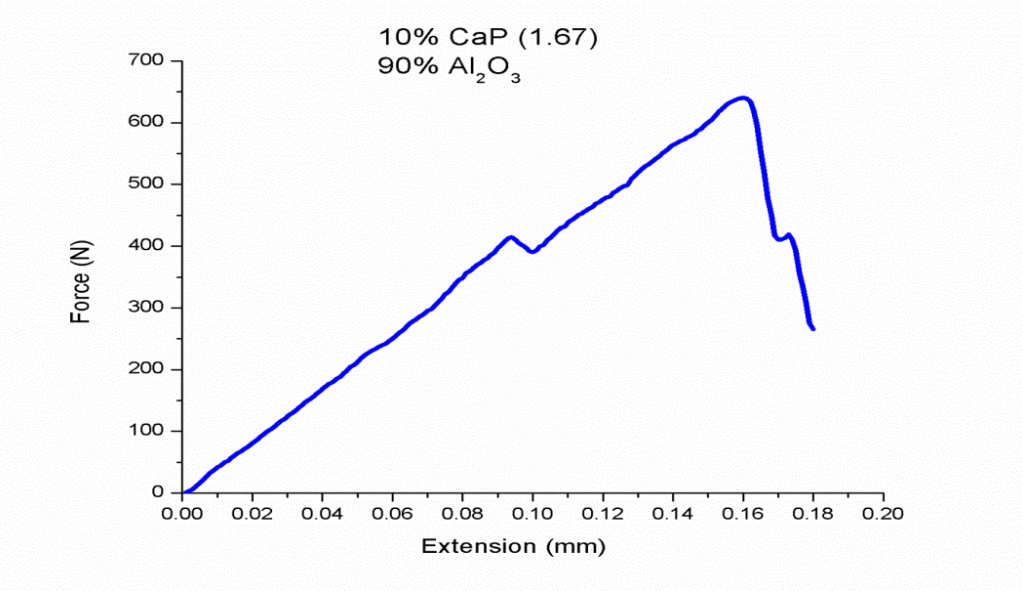

Fig 4.7b: Bi-Axial Flexural strength for (10% CaP(1.67) -90% Al_2O_3) sintered composite

The load vs extension curve for 10% CaP(1.8)- 90% Al_2O_3 compact is shown in figure 4.7c.

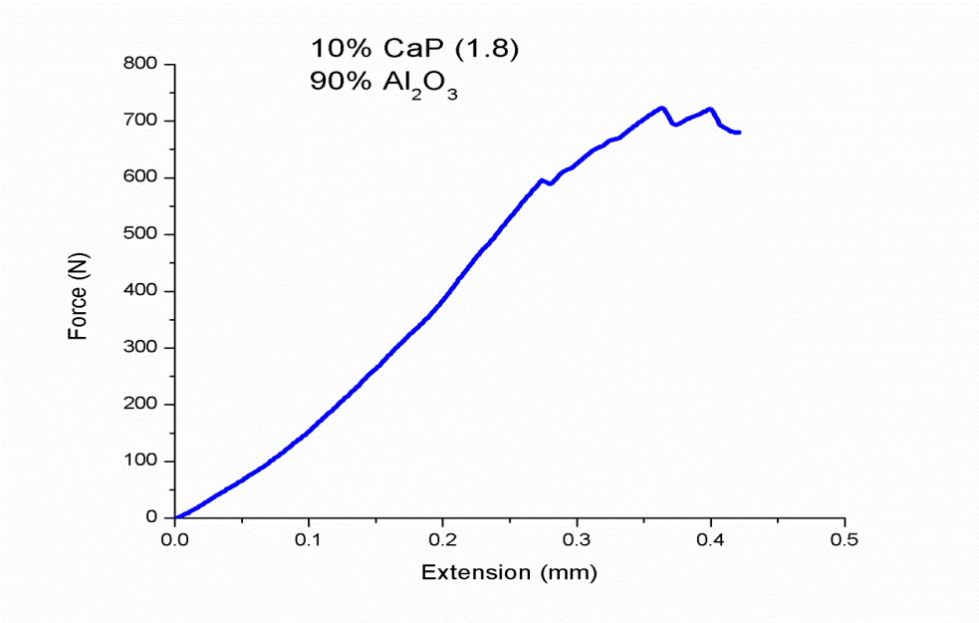

Fig 4.7c: Bi-Axial Flexural strength for (10% CaP(1.8)- 90% Al_2O_3) sintered composite

The load vs extension curve for 20% CaP(1.67)- 80% Al_2O_3 compact is shown in figure 4.7d.

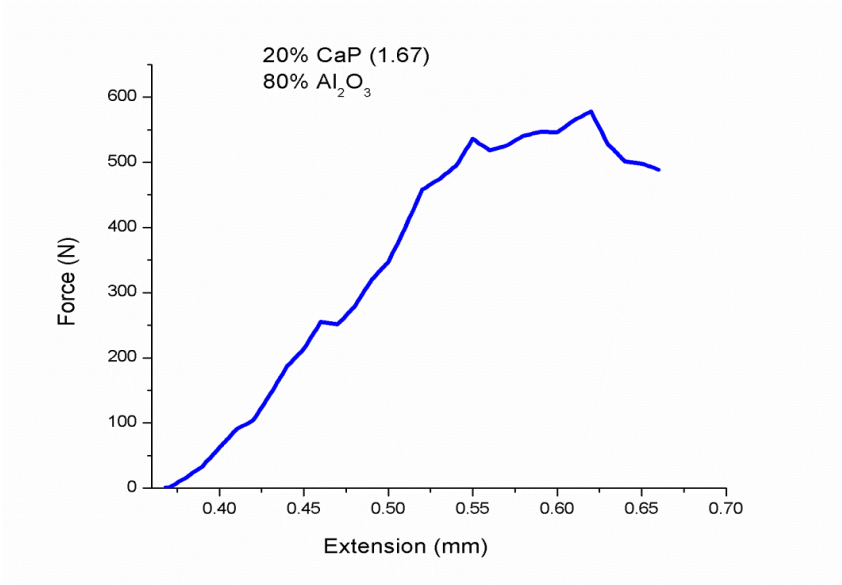

Fig 4.7d: Bi-Axial Flexural strength for (20% CaP(1.67)- 80% Al_2O_3) sintered composite

Bi-Axial Flexural strength of different sintered composites is shown in table 4.2.

Sample No.	Composite	Bi-Axial Flexural Strength (MPa)
2	5% CaP(1.67) 95% Al_2O_3	47.545
1’	10% CaP(1.8) 90% Al_2O_3	23.23
2’	10% CaP(1.67) 90% Al_2O_3	24.14
2’’	20% CaP(1.67) 80% Al_2O_3	19.84

Table 4.2: Bi-Axial Flexural strength of different sintered composites

4.8 SEM of sintered composites:

SEM images of few sintered calcium phosphate –alumina composites are shown in figure 4.8a to 4.8c. The SEM image for 5% CaP(1.8) -95% Al_2O_3 compact is shown in figure 4.8a.

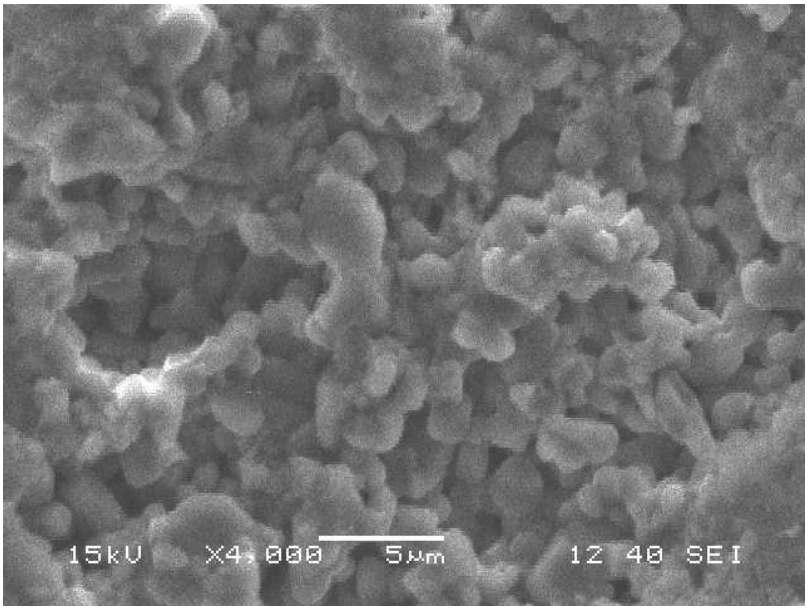

Fig 4.8a: SEM image of 5% CaP (1.8) -95% Al_2O_3 sintered composite

The SEM image for 5% CaP(1.67) 95% Al_2O_3 compact is shown in figure 4.8b.

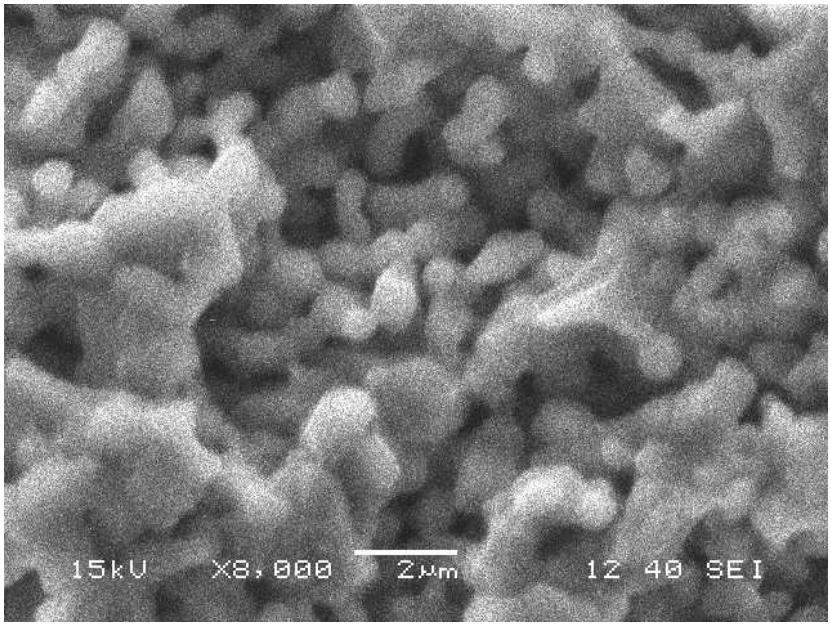

Fig 4.8b: SEM image of 5% CaP (1.67) 95% Al_2O_3 sintered composite

The SEM image for 10% CaP(1.67) 90% Al_2O_3 compact is shown in figure 4.8c.

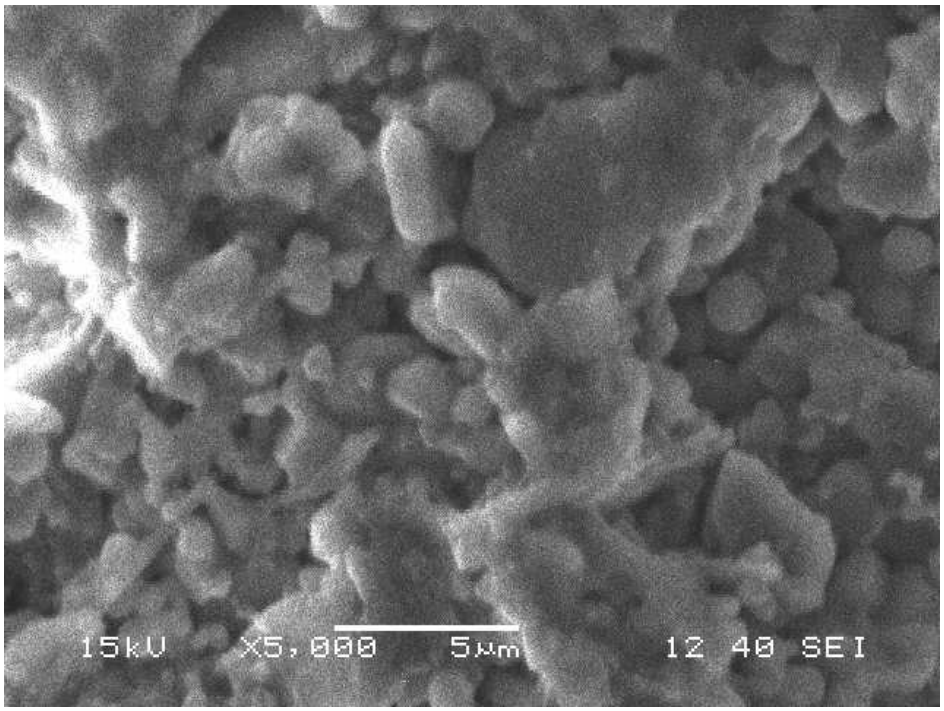

Fig 4.8c: SEM image of 10% CaP (1.67) 90% Al_2O_3 sintered composite

From the SEM images it is seen that, the average grain size of the sintered Calcium phosphate –Alumina composites is around 1µm and to some extent the microstructure shows open porosity in all the samples.

CHAPTER 5

CONCLUSIONS & SCOPE OF FUTURE WORK

Alumina –calcium phosphate composites with different Ca/P moalr ratio and variation in weight % of Calcium phosphate and alumina from 5:95 to 20:80 were successfully processed and characterized. Particle size of calcium phosphate nanoparticles measured using dynamic light scattering (DLS) technique showed size distribution between 100 to 200 nm. Calcium phosphate nanopowder with Ca/P ratio of 1.67 showed the lowest particle size of 127.6 nm. The composition of 5 wt% CaP (1.67) and 95 wt% Al_2O_3 showed the highest bulk density of 3.76 g/cc, the lowest porosity of 11%, the highest Vicker's hardness of 335 HV and the highest flexural strength of 47.545 MPa. In-vitro bioactivity study using osteoblast cell line would be the next characterization step for all the alumina- calcium phosphate composites.

REFERENCES

1. Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E., 2004 "Biomaterials Science, An Introduction to Materials in Medicine, 2nd edition", (Elsevier Academic Press, San Diego) pp.162

2. C. Combes , C. Rey. Amorphous calcium phosphates: Synthesis, properties and uses in biomaterials*. Acta Biomaterialia 6 (2010) 3362–3378*

3. Prashant N. Kumta , Charles Sfeir , Dong-Hyun Lee , Dana Olton , Daiwon Choi . Nanostructured calcium phosphates for biomedical applications: novel synthesis and characterization.
   Acta Biomaterialia 1 (2005) 65–83

4. A. Amera, A. M. A. Abudalazez, A. Rashid Ismail , N. Hayati Abd, Razak, S. Malik Masudi, S. Rizal Kasim, Z. Arifin Ahmad. *Science of Sintering, 43 (2011) 183-192*

5. Preparation and Properties of Nanoparticles of Calcium Phosphates With Various Ca/P ratios
   J. Res. Natl. Inst. Stand. Technol. 115, 243-255 (2010)

6. J. Chandradass & Dong-Sik Bae. Synthesis and Characterization of Alumina Nanoparticles by Igepal CO-520 Stabilized Reverse Micelle and Sol-Gel Processing. *Materials and Manufacturing Processes, 23: 494–498, 2008*

7. Janbey, A.; Pati, R.K.; Tahir, S.; Pramanik, P. A new chemical route for the synthesis of α -Al2O3. J*. European Ceramic Society 2001, 21, 2285–2289.*

8. Li, J.G.; Sun, X.D. Synthesis and sintering behavior of a nanocrystalline -Al2O3 powder. *Acta Materialia 2000, 48, 3103–3112.*

9. Awatef Guidara, Kamel Chaari, Jamel Bouaziz. Elaboration and Characterization of Alumina-Fluorapatite Composites*. Journal of Biomaterials and Nanobiotechnology, 2011, 2, 103-113*

10. S. Kim, Y. M. Kong, I. S. Lee and H. E. Kim, "Effect of Calcinations of Starting Powder on Mechanical Properties of Hydroxyapatite-Alumina Bioceramic Composite," Journal of Materials Science*: Material Medical, Vol. 13, 2002, pp. 307-310. doi:10.1023/A:1014019103240*